

Investigating the nuclear Schiff moment of ^{207}Pb in ferroelectric PbTiO_3

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Abstract. A positive experimental measurement of the nuclear Schiff moment would have important implications for physics beyond the standard model. To aid in the interpretation of a proposed experiment to measure the nuclear Schiff moment of ^{207}Pb in the ferroelectric PbTiO_3 , three-dimensional Hartree-Fock calculations have been performed to model the local electronic structure in the vicinity of the Pb nucleus. The energy shift due to the Schiff moment is found to be a factor of 2 smaller in comparison to existing estimates.

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1. Introduction

The search for the permanent electric-dipole moment (EDM) of quantum particles has been of continued interest for over 40 years since the discovery of the violation of the combined symmetry of charge conjugation (C) and parity (P) in the decay of the K^0 meson [1]. By the CPT theorem, the existence of CP -violation also implies that time-reversal (T) symmetry is violated [2]. P -violation, together with T -reversal asymmetry gives rise to a permanent electric-dipole moment of a quantum system in a stationary state. Therefore ongoing searches for EDM's of elementary particles, nuclei, atoms and molecules are important for studies of fundamental symmetries [3] and they provide important constraints on theories that attempt to go beyond the standard model [4].

Currently, no EDM has been experimentally observed. Experiments on paramagnetic atoms provide the best upper limit on the electron EDM, with the most stringent limitation coming from experiments with atomic thallium [5] and the YbF molecule [6]

$$\begin{aligned} \text{Tl :} \quad d_e &< 1.6 \times 10^{-27} e \text{ cm.} \\ \text{YbF :} \quad d_e &< 1.05 \times 10^{-27} e \text{ cm.} \end{aligned} \quad (1)$$

For diamagnetic atoms, the most EDM sensitive experiment has been performed with mercury vapour, ^{199}Hg , giving an upper limit for the EDM of the ^{199}Hg atom of [7],

$$d(^{199}\text{Hg}) \leq 3.1 \times 10^{-29} e \text{ cm.} \quad (2)$$

For diamagnetic atoms the major contribution to the electron dipole moment is from the nuclear Schiff moment (NSM), \mathbf{S} . The NSM can be defined by the P- and T-odd electrostatic potential [8],

$$\varphi(\mathbf{r}) = 4\pi(\mathbf{S} \cdot \nabla)\delta(\mathbf{r}). \quad (3)$$

The result of [7] has been interpreted with the aid of calculations [9, 10] to yield an upper limit of the Schiff moment of the ^{199}Hg nucleus of,

$$S(^{199}\text{Hg}) < 0.8 \times 10^{-26} e a_B^3, \quad (4)$$

where a_B is the Bohr radius.

Currently, there is intense interest in exploring physical systems that potentially can provide orders of magnitude increases in sensitivity to CP violating effects. As first discussed by Shapiro [11], condensed matter systems are particularly promising in this regard. The electron's EDM is aligned with the spin of the electron, and therefore its magnetic moment. It follows that in a compound with uncompensated spins, the application of an external electric field will align the EDM's and thus align the magnetic moments, giving rise to a macroscopic magnetization. Experiments then aim to measure the reversal of the magnetization by reversing the direction of the external electric field. Recent efforts have focused on gadolinium garnets [12, 13, 14, 15] and more recently on the ceramic $\text{Eu}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ [16, 17, 18, 19].

Similarly to the atomic case, condensed matter systems without unpaired electrons should also be sensitive to the NSM. Ferroelectric PbTiO_3 was proposed for searches

of time reversal symmetry violations enhanced by the internal electric field [20]. Experiments with this compound can potentially lead to improvement of sensitivity to the sNSM by several orders of magnitude in comparison with existing results [21, 22, 23, 24, 25].

The NSM can be detected experimentally either by a measurement of the macroscopic magnetization induced by an electric field or by nuclear magnetic resonance. The lead nuclei will interact with the large internal electric field in the ferroelectric leading to a P, T-odd energy shift. Here, we perform three-dimensional Hartree-Fock calculations in order to model the local electronic structure of PbTiO_3 around the Pb nucleus and determine the energy shift caused by the NSM.

2. Model calculations

PbTiO_3 is an ionic crystal made up of Pb^{2+} , Ti^{4+} and O^{2-} ions. In the ferroelectric phase, PbTiO_3 is tetragonal with $c/a = 1.065$, $a = 3.902\text{\AA}$, $c = 4.156\text{\AA}$ [26], with Pb^{2+} and Ti^{4+} displacements of 0.47\AA and 0.30\AA respectively [27]. The ion displacements are in accordance with the Schiff theorem [28]. The lattice relaxes so as to screen the strong internal ferroelectric field such that the average field that acts on each charged particle in the compound is zero. However, the finite size of the ions plays an important role, with oxygen electrons (s and p -wave) penetrating into the core of the Pb ion in the PbO_{12} cluster (Fig. 1). Due to the displacement of the Pb ion, this creates an electric field gradient at the Pb nucleus. The NSM interacts with this gradient, leading to an energy shift. The energy shift can be calculated using second order perturbation

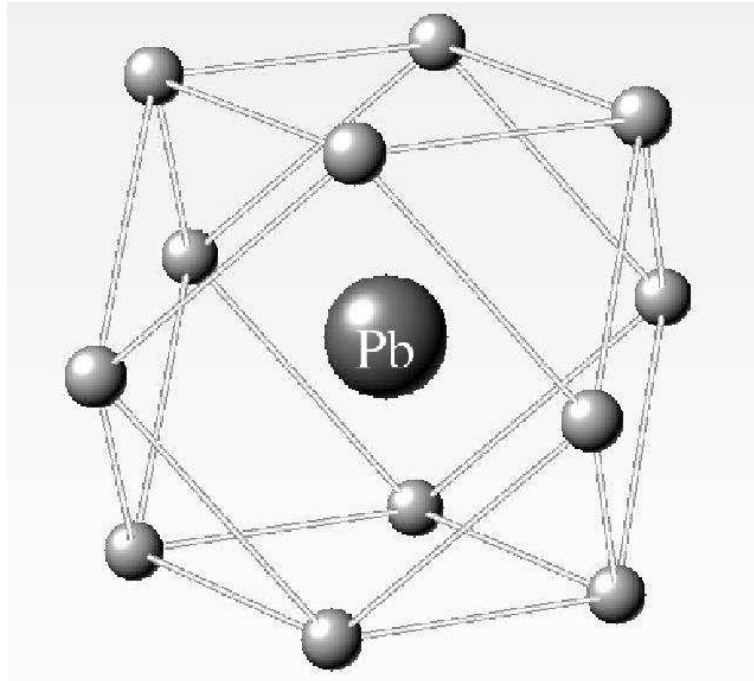


Figure 1. The Pb^{2+} ion surrounded by the first coordination sphere of 12 O^{2-} ions.

theory. In Ref. [13], using a semiclassical approximation for the electron wavefunctions, a formula for the energy correction due to the NSM was obtained,

$$\Delta\epsilon/E_0 \simeq b \frac{Z^2}{(\nu_s\nu_p)^{3/2}} \left(\frac{1}{3}R_{1/2} + \frac{2}{3}R_{3/2} \right) \frac{(\mathbf{X} \cdot \mathbf{S})}{a_B e a_B^3}, \quad (5)$$

where $\Delta\epsilon$ is the energy shift caused by the NSM \mathbf{S} [29], \mathbf{X} is the ion displacement, $E_0 = 27.2$ eV, $e = |e|$ is the charge of the electron, $Z = 82$ is the nuclear charge of Pb, ν_s and ν_p are effective principal quantum numbers and $b = 16\beta/\sqrt{3}$. β is a parameter describing lead orbitals partially occupied by oxygen electrons. $R_{1/2}$ and $R_{3/2}$ are relativistic enhancement factors [3, 13] given by,

$$R_{1/2} = \frac{4\gamma_{1/2}x_0^{2\gamma_{1/2}-2}}{[\Gamma(2\gamma_{1/2}+1)]^2}$$

$$R_{3/2} = \frac{48\gamma_{1/2}x_0^{\gamma_{1/2}+\gamma_{3/2}-3}}{\Gamma(2\gamma_{1/2}+1)\Gamma(2\gamma_{3/2}+1)}, \quad (6)$$

where $\gamma_{1/2} = \sqrt{1 - Z^2\alpha^2}$, $\gamma_{3/2} = \sqrt{4 - Z^2\alpha^2}$, α is the fine structure constant, $\Gamma(x)$ is the gamma function and $x_0 = (2Zr_0/a_B)$, with r_0 the nuclear radius.

An understanding of the order of magnitude of this energy shift can be gained by considering that the energy shift can be approximated by the product of the internal electric field in ferroelectric PbTiO_3 , $E_{int} \simeq 10^8$ V/cm, and the EDM of the Pb^{2+} ion, $d(\text{Pb}^{2+})/(e\text{ cm}) \simeq 10^{-2}S/(ea_B^3)$, where we have assumed that the EDM of the Pb^{2+} ion is similar to that of the Hg atom. This gives, $\Delta\epsilon \simeq E_{int}d(\text{Pb}^{2+}) \simeq 10^6 \frac{S}{ea_B^3}$ eV [22].

In Ref. [21], Eq. (5) was applied to calculate the energy shift using a value of $\beta = -0.29$ estimated previously for GdO_8 clusters [13].

This gave an estimate for the energy shift of,

$$\Delta\epsilon \simeq -1.1 \times 10^6 \frac{S}{ea_B^3} \text{ eV}. \quad (7)$$

The method used to calculate β involved matching a linear combination of the electron wavefunctions of the $2p_\sigma$ electrons of O^{2-} possessing the correct cubic symmetry, with single particle $6s$ and $6p$ states of the central Gd^{3+} ion that can be thought of as being occupied by the oxygen electrons. The matching is done at an intermediate distance in the cluster between the O^{2-} ions and the central Gd^{3+} ion.

Aside from the desirability of using a value of β calculated specifically for the PbO_{12} cluster, the fact that this cluster is closed shell and free from complications arising from open shell effects allows a more accurate method of calculating β to be used in order to benchmark the earlier estimates. By relating β to a shift in the electron density around the Pb nucleus, the calculation of β , and thus the energy shift due to the NSM, is reduced to determining the electron density of the PbO_{12} cluster. This allows the well-developed theoretical apparatus of quantum chemistry to be applied. Once a ground state wavefunction is obtained via the Hartree-Fock approximation, the density shift around the Pb nucleus can be simply extracted.

First we relate the density shift to β . $\Delta\rho(z)$ will be defined as the electron density shift around the lead nucleus due to the displacement of the lead ion from the center

of the PbO_{12} cluster, z is the distance from the lead nucleus in the direction of the displacement. This can be represented by,

$$\Delta\rho(z) = \frac{\rho(z) - \rho(-z)}{2}. \quad (8)$$

It is possible to make a simple estimate of the density shift as follows. Near the Pb^{2+} ion the electrostatic potential for electrons is dominated by that of the central Pb^{2+} ion. Therefore the wavefunctions of electrons in this region can be well described by partially occupied Pb^{2+} orbitals. The interaction of electrons with the NSM of Pb is highest near the Pb nucleus. The largest contribution to this interaction comes from s - and p -wave states that can penetrate close to the nucleus. First we let $|S\rangle$ and $|P\rangle$ be a combination of the p_σ states of the PbO_{12} cluster that have s - and p -wave symmetries with respect to the centre of the cluster. Then these states can be represented as partially occupied $7s$ and $6p$ orbitals of the central lead ion.

$$|S\rangle \rightarrow \beta_S|7s\rangle, \quad |P_i\rangle \rightarrow \beta_P|6p_i\rangle, \quad (9)$$

where $i = \{x, y, z\}$. When the Pb ion is shifted from the centre of the cluster, the $|S\rangle$ and $|P\rangle$ states no longer have exact s and p -wave symmetries with respect to the lead ion but are instead a mixture of the two. If we assume the linear approximation, then the admixture of states of different parity due to the displacement \mathbf{X} of the Pb^{2+} ion is of the form,

$$\begin{aligned} |S\rangle &\rightarrow \beta_s|7s\rangle + \sum_i \beta'_s \frac{X_i}{a_B} |6p_i\rangle \\ |P_i\rangle &\rightarrow \beta_p|6p_i\rangle + \sum_i \beta'_p \frac{X_i}{a_B} |7s\rangle. \end{aligned} \quad (10)$$

The change in the density due to the displacement of the Pb^{2+} ion along the z direction is then,

$$\Delta\rho(z) = 4\beta \frac{X}{a_B} \psi_{7s}(z) \psi_{6p}(z), \quad (11)$$

where $\beta = (\beta_s \beta'_s + \beta_p \beta'_p)$ and a factor of 2 comes from the double occupancy of each spin orbital.

In order to obtain the electron density in the vicinity of the lead nucleus, we adopt a simple model of the electronic structure with only the Pb^{2+} ion and the 12 O^{2-} ions in the first coordination sphere of the Pb^{2+} ion being included *ab-initio*. The 12 O^{2-} ions are placed at the mid-points of the edges of a cube of length 4\AA . The Pb^{2+} ion is displaced by a distance X from the centre of the cube and 8 Ti^{4+} ions (see below) are represented by point charges displaced from the corners of the cube by $0.3X/0.5$. Varying the Pb ion displacement will then also change the Ti ion displacement, this will model a change in the strength of the internal ferroelectric field. Point charges are also added to ensure that the system is neutral. These charges are placed at the positions of the 24 O^{2-} ions surrounding the PbO_{12} cluster.

The GAMESS-US quantum chemistry code [30] is used to perform Hartree-Fock calculations for PbO_{12} . The WTBS basis [31, 32] set is used for all calculations presented

here. A diffuse sp shell is also added to the Pb^{2+} and O^{2-} orbitals in order to better represent the ionic bonds present in this system. A trial wavefunction is built from Pb^{2+} and O^{2-} Hartree-Fock wavefunctions, where in both cases the ions are enclosed by a cubical array of point charges. For O^{2-} this is necessary in order to obtain a stable ground state in the Hartree-Fock approximation. This trial wavefunction is then used as a starting approximation to obtain a converged Hartree-Fock wavefunction for the PbO_{12} cluster. Using a converged Hartree-Fock wavefunction for the PbO_{12} cluster, the density shift around the Pb nucleus can be calculated, and then via Eq. (11) used to obtain a value of β . The energy shift due to the NSM is then found via Eq. (5).

3. Results

In order to test the various assumptions made in the present model, a number of calculations have been carried out. Firstly, the point charges representing the Ti ions are treated here as an adjustable parameter in order to assess the dependence of the final result on the crystal structure, with calculations carried out for a range of Ti charges. Secondly, the assumed linearity of the density shift is tested by carrying out calculations for a number of Pb displacements.

First, to illustrate how well Eq. (11) performs in capturing the essential physics of the density shift, $\Delta\rho$ as a function of the distance from the Pb nucleus is plotted in figure 2 for a Ti charge of $+3.5$. We match the numerical density shift to the analytical expression of Eq. (11) using atomic Hartree-Fock wavefunctions for the $6p$ and $7s$ states of Pb^{2+} , treating β as an adjustable parameter. The matching is done at points up to the first node, and then an average value of β is taken. As is clear, the analytical expression agrees well with the numerical results.

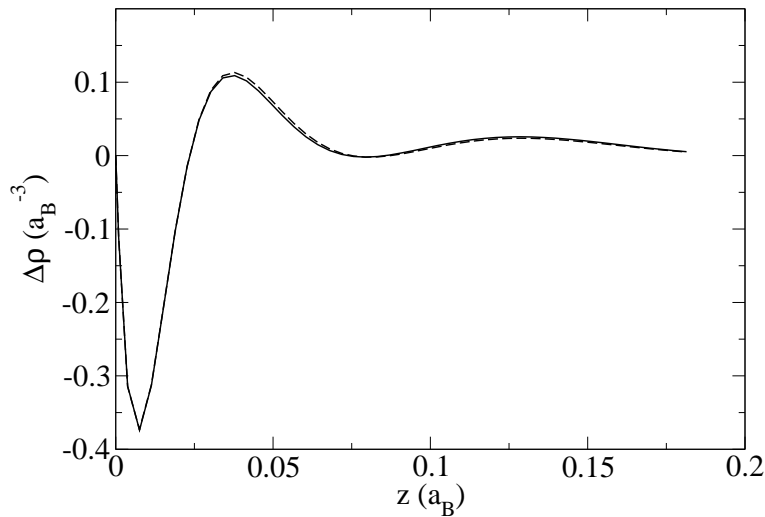


Figure 2. $\Delta\rho(z)$ for $X=0.5\text{\AA}$, $q = +3.5$. Solid line, GAMESS-US; dashed line, Eq. (11) with $\beta = -0.125$.

Next, the validity of the linear approximation for the density shift is investigated. Figure 3 plots $\Delta\rho$ at distances from the Pb nucleus corresponding to the first minimum and maximum of $\Delta\rho$, as a function of the Pb^{2+} ion displacement. From the figure, it is seen that a Ti charge of 3.5 gives the best agreement with the linear approximation out to $X = 0.5\text{\AA}$, with some deviation from linearity observed for charges of 3.0 and 4.0.

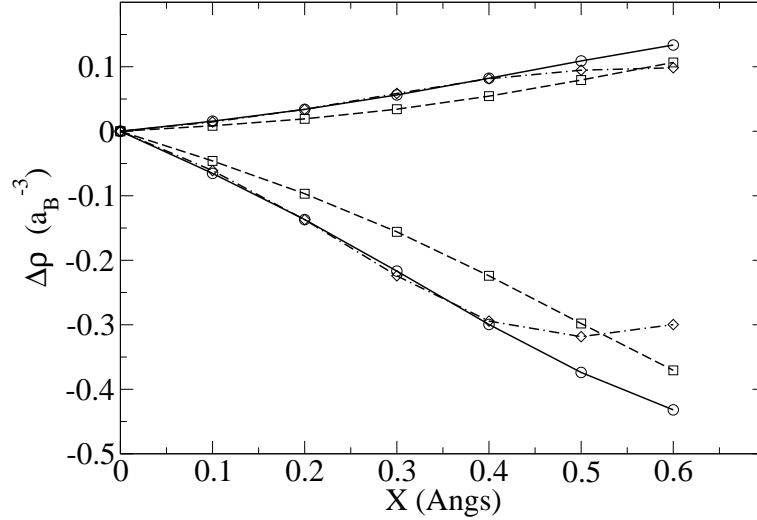


Figure 3. Density shift as a function of the Pb ion displacement X , (with Ti charges displaced by $0.3X/0.5$) for varying Ti charges q . Dashed line, $q = +3.0$; solid line, $q = +3.5$, dot-dashed, $q = +4.0$. Lower lines at $z = 0.004\text{\AA}$, upper lines at $z = 0.02\text{\AA}$

Finally, β as a function of the Ti charge is plotted in figure 4 for a Pb^{2+} displacement of $X = 0.5\text{\AA}$. It is seen that for Ti charges between +3 and +4, β ranges from -0.1 to -0.125, demonstrating that β does not depend strongly on the crystal structure. This compares to a previous estimate of $\beta = -0.29$ [21, 22] used for PbTiO_3 that was originally derived for the garnet structure of a Gd^{3+} ion enclosed by eight O^{2-} ions [13]. Taking a value of $\beta \simeq -0.125$ for a Ti charge of +3.5 as an upper limit for $|\beta|$, Eq. (5) is evaluated for a Pb displacement of 0.47\AA , with effective principal quantum numbers of the $6p$ and $7s$ states of Pb^{2+} , derived from Hartree-Fock energies of 1.028 and 1.417 respectively [33]. The nuclear radius, r_0 , of ^{207}Pb is estimated by the approximation, $r_0 = CA^{1/3}$, where A is the atomic mass number and $C = 1.25 \times 10^{-15}$ m. This gives $r_0 \simeq 7.39 \times 10^{-15}$ m. The resulting energy shift is then found to be,

$$\Delta\epsilon \simeq -0.66 \times 10^6 \frac{(\mathbf{X} \cdot \mathbf{S})}{a_B e a_B^3} \text{ eV} = -0.59 \times 10^6 \frac{S}{e a_B^3} \text{ eV}. \quad (12)$$

This is approximately two times lower than the existing estimate, see Eq. (7).

4. Conclusions

The work in this paper is part of a continuing theoretical and experimental programme in aid of experimental investigations of CP violating effects in condensed matter systems.

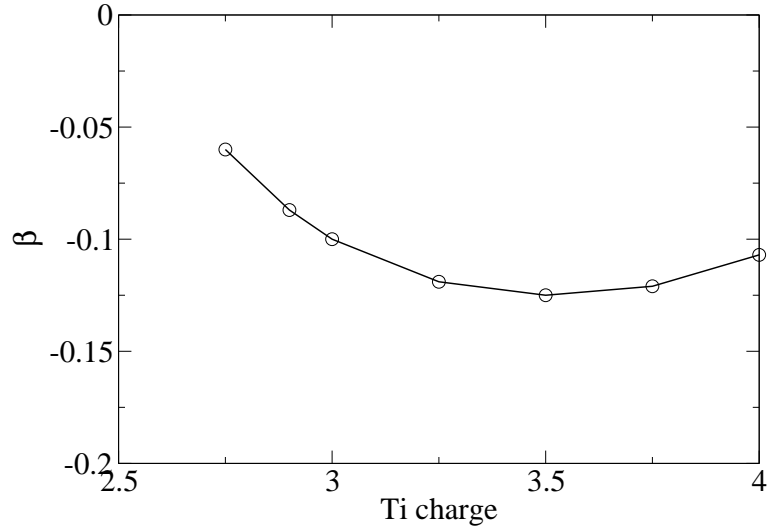


Figure 4. β as the Ti charge is varied for $X = 0.5\text{\AA}$.

A Hartree-Fock calculation of the PbO_{12} cluster enabled the density shift around the Pb nucleus due to the penetration of the oxygen electrons into the Pb ion to be calculated. From this an energy shift was calculated that is almost a factor of 2 lower than a previous estimate.

There are two areas in the current work that merit further investigation. Firstly, the effect of the potential due to the crystal field needs to be properly taken into account. A possible solution to this issue is via the CRYSTAL code [34, 35]. This particular code uses linear combinations of atom centred Gaussian functions to perform both Hartree-Fock and a variety of density functional theory calculations. This would allow a good description of both the crystal structure and also the penetration of the O electrons into the Pb ion. An existing calculation using the CRYSTAL code has provided accurate structural and electronic properties of PbTiO_3 [36].

Secondly, relativistic effects due to the heavy Pb nucleus need to be taken into account in order to correctly describe the behaviour of O electrons close to the Pb nucleus. As a first step, this can be done by solving the Dirac-Fock equations for the PbO_{12} cluster. A challenge here will be in converging the self-consistent 4-component Dirac-Fock equations for such a large system. The BERTHA [37] or DIRAC codes [38] can be investigated for this purpose.

These two phenomena that must be included in any complete treatment of the problem, namely the potential due to the crystal lattice and relativistic effects due to the high nuclear charge of the Pb nucleus, make this a highly demanding theoretical and computational problem.

A positive experimental finding of the nuclear Schiff moment would be of great importance to the entire physics community. Theoretical input into the design and interpretation of future experiments will be crucial in this effort. As such, we hope that the present model calculations will prompt renewed theoretical interest in this field.

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